

ESR study of atomic hydrogen and tritium in solid T₂ and T₂:H₂ matrices below 1K

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(Dated: September 22, 2016)

We report on the first ESR study of atomic hydrogen and tritium stabilized in a solid T₂ and T₂:H₂ matrices down to 70 mK. The concentrations of T atoms in pure T₂ approached $2 \times 10^{20} \text{ cm}^{-3}$ and record-high concentrations of H atoms $\sim 1 \times 10^{20} \text{ cm}^{-3}$ were reached in T₂:H₂ solid mixtures where a fraction of T atoms became converted into H due to the isotopic exchange reaction $\text{T} + \text{H}_2 \rightarrow \text{TH} + \text{H}$. The maximum concentrations of unpaired T and H atoms was limited by their recombination which becomes enforced by efficient atomic diffusion due to a presence of a large number of vacancies and phonons generated in the matrices by β -particles. Recombination also appeared in an explosive manner both being stimulated and spontaneously in thick films where sample cooling was insufficient. We suggest that the main mechanism for H and T migration is physical diffusion related to tunneling or hopping to vacant sites in contrast to isotopic chemical reactions which govern diffusion of H and D atoms created in H₂ and D₂ matrices by other methods.

PACS numbers: choose

I. INTRODUCTION

The solid hydrogens are among the simplest quantum crystals. Small masses and weak interactions result in a dramatic influence of quantum effects on their properties. Light impurities of the atomic hydrogens introduced into such host matrices turned out to be mobile and able to diffuse by the repetition of quantum exchange reactions [1]. It might be expected that reducing the distance between unpaired hydrogen atoms in the matrix by accumulating them to high concentrations may lead to a number of fascinating phenomena related to quantum degeneracy or to emergence of a strong exchange interaction between electron clouds and possible conductivity of the matrix.

A number of methods are available for producing unpaired atoms inside the molecular hydrogen solids. Among them are condensing of rf-discharge products onto liquid-helium cooled surfaces [2] or directly into superfluid helium [3, 4], γ -irradiation [5] or adding small amounts of β -radioactive tritium into an initial gas mixture. The highest densities of H in H₂ above 1 K have been obtained with the latter method, $7 \times 10^{18} \text{ cm}^{-3}$ with a 2% T₂ admixture [6], while densities approaching 10^{20} cm^{-3} were reached in pure tritium [7]. The method where β -decay of tritium produces free radicals was pioneered by Lambe [8] who studied radiation induced defects in solid T₂ and by Sharnoff and Pound who studied accumulation and dynamic nuclear polarization of D in solid D₂ [9]. First experiments below 1 K before our work were carried out by Webeler [10], who conducted a calorimetric study of H₂ with a 0.02% tritium admixture in a range of 0.2-0.8 K. Both spontaneous and stimulated heat spikes of the sample cell temperature were detected

and attributed to collective recombination of H atoms in the H₂ matrix. Collins et al. [11] repeated Webeler's experiment using ESR as a detecting tool at a temperature of 1.2 K and confirmed that the heat spikes are also accompanied by abrupt *en masse* atomic recombination. Mapoles et al. [12] detected spectacular light emission in their D-T (50% DT, 25% D₂ and 25% T₂) samples which was also assigned to explosive recombination of atoms. The atomic concentrations achieved in the experiments of Webeler were estimated indirectly as $5 \times 10^{17} \text{ cm}^{-3}$, while in following theoretical works, Zeleznik [13] and Rosen [14] hypothesized that they could be significantly increased if the storage temperature would be lowered. These theoretical conclusions were supported by Collins et al. who used X-band ESR for studying deuterium and tritium atoms in solid D-T mixtures at temperatures 2.1-10 K and found a strong dependence of the steady state concentration of atoms on storage temperature [7].

Another method for producing high concentrations of H atoms was recently employed by Ahokas et al. [15], [16] who used a cryogenic rf discharge to dissociate H₂ molecules in solid films *in situ* and reached H concentrations $\simeq 2 \times 10^{19} \text{ cm}^{-3}$ at 0.5 K. Later it was demonstrated that even higher concentrations of atomic hydrogen can be produced in H₂:D₂ mixtures where deuterium atoms become converted into H in the course of the isotopic exchange reactions $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$ and $\text{D} + \text{HD} \rightarrow \text{D}_2 + \text{H}$ [17].

Similar to the lighter counterparts, the isotopic exchange reactions of hydrogen and deuterium with tritium (1) and (2) should proceed in T₂:H₂(D₂) matrices.



The rates of these reactions in the gas phase were calculated by Truhlar et al. [18] and later by Aratono et al. [19] who predicted an extremely high rate of the reaction (1) at low temperatures, $k^{ex} \sim 2 \times 10^{-25} \text{cm}^3 \text{s}^{-1}$, and a two order of magnitude smaller rate for the reaction (2). The only experimental observation of the isotopic exchange reactions (1) and (2) at low temperatures so far was done by Aratono et al. [20] who studied them in superfluid helium where they produced T atoms from ^3He *in situ* by neutron bombardment. The authors were unable to deduce the absolute reaction rates, but reported on the isotope effect when H is replaced with D in the reactions (1) and (2). For the reaction (1) it was measured to be $k_{\text{H}_2}^{ex}/k_{\text{D}_2}^{ex} \approx 150$, while for reaction (2) $k_{\text{TH}}^{ex}/k_{\text{TD}}^{ex} < 19.6$. Reactions similar to (1) and (2) involving deuterium and tritium atoms should proceed much slower than those for hydrogen because of smaller zero-point energies of the reactants. This was also supported by the only experimental study of D and T atoms in a D-T matrix carried out by Collins et al. [7] at $\text{T}=2.1 \text{ K}$ who reported on the absence of T-to-D conversion in their samples. The authors estimated the total atomic concentrations to be $\sim 10^{20} \text{cm}^{-3}$ with a possible uncertainty $\sim 50\%$. Studying the mixtures of T and H in this work we found that the isotopic exchange reaction (1) proceeds with a much higher rate than reaction (2). We estimate the rate of the reaction (1) to be $k = 3(2) \times 10^{-26} \text{cm}^3 \text{s}^{-1}$.

The main purpose of these experiments was to examine opportunities for reaching the highest possible concentrations of atomic species using the β -decay of tritium. We performed the first quantitative ESR study of T and H atoms stabilized in thin tritium films at temperatures below 1 K down to 70 mK. The record-high concentrations of T atoms in pure T_2 approaching $2 \times 10^{20} \text{cm}^{-3}$ and concentrations of H atoms of about $1 \times 10^{20} \text{cm}^{-3}$ in solid $\text{T}_2 : \text{H}_2$ were reached. It turned out that in the films thicker than 100 nm, maximum achievable density of H and T was limited by a spontaneous and stimulated explosive recombination of atomic species. The explosion threshold density and periodicity turned out to be strongly dependent on the storage temperature. Decreasing the film thickness below 100 nm allowed us to avoid explosions, but the maximum density was also somewhat reduced due to less effective use of the electrons for dissociation of molecules.

II. EXPERIMENTAL

A. Setup

The experiments were performed in the sample cell (SC) shown in Fig.1 with further details described in [21]. The SC is located at the center of a 4.6 T superconducting magnet and is attached to the mixing chamber of an Oxford 2000 dilution refrigerator. The main investigation tools in our experiments are a 128 GHz ESR spectrometer and a quartz-crystal microbalance (QM) able to measure the film thickness with a 0.2 monolayer accuracy. The ESR resonator (Q=5700 at 300 mK) has an open Fabry-Perot geometry which made it possible to install beam lines for condensing films of hydrogen isotopes onto the QM and provide a flux of atomic hydrogen created in a specially constructed H-gas source. Three auxiliary rf resonators for performing electron-nuclear double resonance (ENDOR) of H, D and T atoms are arranged near the QM. Only one of them, the H NMR coil, is shown in Fig.1. A capillary for condensing the molecular hydrogen comes directly from the room temperature gas handling system and it is kept above the tritium boiling temperature during condensing of the film by driving current through electrical heaters. A special source of cold hydrogen gas is arranged at the top of the sample cell body and connected to it via a stainless steel tubing system. The gas of H atoms is very useful for calibration of the absolute number of spins detected by our ESR spectrometer as well as for the accurate measurement of the magnetic field and the ESR line shifts [21]. The source can be also used for obtaining a flux of molecular hydrogen, which was not used in the present work.

A Ru-oxide bolometer is arranged in close proximity to the sample to measure the heat released during explosive recombination. The bolometer was suspended on fine superconducting wires which assure only a weak thermal coupling to the sample cell body. The bolometer has a negligibly small heat capacity and even tiny amounts of heat can quickly raise its temperature above the temperature of the sample cell.

B. Procedure

The technique of condensing hydrogen onto a cold surface via the long and sufficiently cold capillary provides a rather efficient way of cleaning the condensed gas from any other contaminants except hydrogen and its isotopes. Therefore, for the experiments described in this work, we have not paid much attention to the chemical purity of T_2 gas, and utilized the most simple and cheap source available. The T_2 gas we used was extracted from commercially available tritium vials produced for use as luminescent fishing floats. Each such 5 mm diameter and 5 cm long vial contained about 5-10 μmoles of T_2 , which

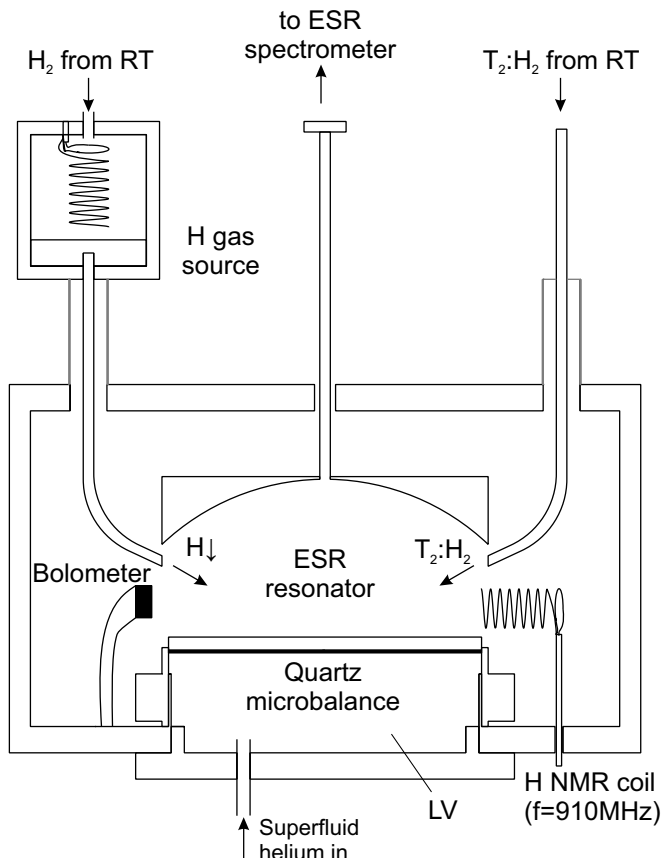


Figure 1. Sample cell schematic. The T and D NMR coils are not shown in the figure

was sufficient for several experiments described in this work. The purity of the gas extracted from the vials was verified using a MKS-Granville-Phillips VQM 835 mass spectrometer with the main concern being the amount of other hydrogen isotopes in it. It turned out that as the main impurity, the gas in the vials typically contained about 15% of HT. It is known that the main impurity in the T_2 gas right after production should be DT ($\sim 1\%$), while significant HT contamination appears during storage[22]. We found that T_2 gas quickly degraded after extracting it from the glass vials. About 20% of it became converted to HT and H_2 after 3 months of storage. In order to minimize the HT content we used only fresh T_2 gas for preparing our samples.

The films of solid molecular tritium and hydrogen were deposited by condensing a few μmol of normal T_2 or $T_2:H_2$ mixtures onto the QM directly from a room temperature reservoir. A small amount of helium ($\sim 1\text{ mmol}$) was condensed into the lower volume (LV in Fig.1) under the quartz microbalance disk in order to have a saturated helium film there. The film flushes the lower surface of the QM and provides an efficient way to remove an excess of heat released during film deposition, recombination of atoms and tritium β -decay. The SC temperature during

sample deposition stayed between 1 and 1.5 K.

Unpaired H and T atoms appeared in the solid films, and were detected by the ESR spectrometer immediately after completing the deposition process. The atoms result from the dissociation of molecules by the 5.7 keV electrons of the T_2 β -decay. We followed the kinetics of the growth of the atomic concentrations during the time interval from several days up to two weeks, periodically recording the ESR spectra and following the QM frequency changes. The SC temperature was stabilized to several different values below 1 K in order to study the sample properties as a function of temperature. It turned out that the presence of tritium introduces substantial heating in the SC and limits minimum attainable temperature to about 150 mK for the films with thickness about 300 nm. The sample cell temperature was also shortly raised by several tens of mK during the magnetic field sweeps due to eddy current heating. This was essential for triggering the explosive recombination in some of the samples. After finishing the measurements for each film, the sample cell and filling capillary were heated to a temperature above 30 K and pumped for several hours in order to evacuate all hydrogen and clean all surfaces before creating a new sample. This cycle was repeated several times for samples of different $H_2:T_2$ composition and thickness.

For calibration purposes we utilized the ability to accumulate the H gas in the main volume of the SC. This is normally done by: 1) condensing a certain amount of molecular hydrogen into the H gas source; 2) condensing small amounts of helium inside the upper volume of the SC and the source, sufficient to form a several nm thick superfluid ^4He film; 3) running the rf discharge in the miniature rf coil inside the H gas source. The gas of atomic hydrogen is produced by dissociation by the electrons of the discharge. The helium film covering the surfaces prevents recombination of the atoms on the SC walls. In the course of the experiments we found that atomic hydrogen gas can be accumulated (with a substantially smaller rate) also without running discharge, once a helium film is present in the SC. This effect was only observed in the experiments with tritium-hydrogen mixtures. It indicates that a fraction of the atoms resulting from H_2 dissociation in solid films by the electrons of the β -decay may be kicked out from the films into the bulk of the SC and get accumulated there. Unfortunately we were unable to observe gas lines of spin-polarized tritium. This is caused by substantially larger adsorption energy for T on helium surfaces and possibility that atomic T may penetrate the helium film. Presence of a helium film in the SC leads to an extra heat load caused by the film re-condensing from the upper parts of capillaries. In order to avoid this disturbance and reach the lowest temperatures most of the experiments described in this work were performed without helium film in the SC.

C. Samples

The main emphasis of this work was placed on reaching the highest-possible concentration of unpaired atoms in hydrogen solids using β -decay of tritium. Aiming on that we tried to find optimal values of two basic parameters of the films: the film thickness and $T_2:H_2$ ratio. We studied both pure tritium films and different mixtures of T_2 and H_2 . We expected that in the latter a significant fraction of T atoms will be converted to H by the chemical exchange reactions (1) and (2). Varying the film thickness we tried to reach a trade-off between more efficient generation of unpaired atoms in thicker films and better cooling expected for thinner samples. A summary of the properties of 6 different samples studied in this work is given in Table I.

A second goal of this work was to study in detail explosive recombination of H and T atoms previously observed in works of Webeler [10] and Collins et al. [11]. Varying the film parameters: thickness and isotope composition as well as sample temperature, we tried to find the conditions for which this process can be suppressed.

First a $1\mu\text{m}$ thick sample of para- H_2 with a 1% tritium admixture was studied at $T=150\text{ mK}$. No signals of atomic tritium were observed while the H concentrations obtained in this sample levelled off at about $1\times 10^{19}\text{ cm}^{-3}$. We did not detect any signatures of explosive recombination of atoms similar to what were reported in [10] and [11] for the bulk samples. This can be explained by a larger surface to volume ratio and much better cooling of our hydrogen films compared to previous experiments. In the work [11] authors reported on suppression of events of spontaneous explosive recombination by providing better cooling to their samples after collecting bulk amounts of liquid helium in the sample cell. The films we studied are rather thin compared to the penetration depth of electrons ($\sim 3.5\mu\text{m}$) released in β -decay of tritium [23] and only a fraction of their kinetic energy, $\langle E_k \rangle = 5.7\text{ keV}$, is dissipated in the film. This reduces the heat released in the samples, but also reduces the rate of dissociation in thin films leading to smaller atomic densities.

Next, we studied films of "pure" T_2 , i.e. without any H_2 added to it prior to condensing. A second sample was a 250 nm pure tritium film, which we studied at the lowest temperature of 160 mK, limited by the heat from tritium decay. In this sample we reached maximum atomic concentrations approaching $2\times 10^{20}\text{ cm}^{-3}$ where most of the atoms were T, with the T:H ratio being about 6:1.

The atomic concentrations in this sample were limited by periodic collective recombination of atoms which raised the SC temperature from 0.16K to about 0.25K. Similar heat spikes were also registered by the bolometer, which has a much faster response time. The spikes were found to appear both while sweeping magnetic field and between the sweeps when the cell was gradually cooling

| | $s, \text{ nm}$ | Composition, % | | | $n\times 10^{19} \text{ cm}^{-3}$ | | | H/(T+H) | |
|----|-----------------|----------------|-------|----|-----------------------------------|------|-------|----------|----------|
| | | T_2 | H_2 | HT | T | H | total | observed | expected |
| 1. | 1000 | 1 | 99 | - | - | 1.0 | 1.0 | 1.00 | 0.99 |
| 2. | 250 | 85 | - | 15 | 15 | 2.5 | 18 | 0.14 | 0.08 |
| 3. | 35 | 85 | - | 15 | 10 | 1.0 | 11 | 0.09 | 0.08 |
| 4. | 80 | 81 | 4 | 14 | 4.2 | 4.5 | 8.7 | 0.53 | 0.11 |
| 5. | 300 | 60 | 29 | 11 | 0.5 | 10.5 | 11 | 0.95 | 0.35 |
| 6. | 250 | 4 | 95 | 1 | - | 2.5 | 2.5 | 1.00 | 0.96 |

Table I. A summary table of the samples studied in this work. Film thickness is denoted as s . Expected values of $H/(T+H)$ ratios were estimated from H_2 and HT content.

down. Collective recombination also resulted in a partial sublimation of tritium films detected by the QM. A fraction of evaporated tritium molecules re-condensed onto the other surfaces of the SC including the spherical mirror.

A different behaviour was observed in a substantially thinner, 35 nm pure T_2 film (sample 3). The accumulation of atoms in the film was not interrupted by their explosive recombination. Condensing a smaller amount of tritium also allowed us to store the sample at temperature of about 80 mK. However, the maximum densities of atoms in the thinner film were a factor of 2 lower than that in Sample 2.

Three samples with different $T_2:H_2$ content were studied to examine the possibility of reaching the highest concentrations of H atoms and possible observation of the exchange reactions between two isotopes. Sample 4: 80 nm $T_2:4\%H_2$, sample 5: $T_2:30\%H_2$ (300 nm) and sample 6: $H_2:5\%T_2$ (360 nm). Total density of atoms was a factor of 2 lower than in thick "pure" tritium sample, but in Sample 5 we succeeded in reaching a record high density of H atoms exceeding 10^{20} cm^{-3} . We observed no explosive atomic recombination in the samples of the $T_2:H_2$ mixture films. All these samples featured a much smaller T:H ratio as compared to the initial content of $T_2:H_2$ which we interpret in terms of the isotope exchange reaction.

D. ESR and ENDOR spectra

ESR spectra were recorded by a cryogenic heterodyne spectrometer which does not utilize field or frequency modulation [24]. In this work we used the CW method of operation, where the frequency of the excitation source is kept constant, while the magnetic field is swept across the resonance. The ESR signal at the output of the detection system contains both components of the complex magnetic susceptibility: absorption and dispersion as a function of the magnetic field sweep. In all our spectra presented below we will show absorption signals only.

The ESR spectrum of atomic hydrogen and tritium contains a doublet of lines separated by a distance equal

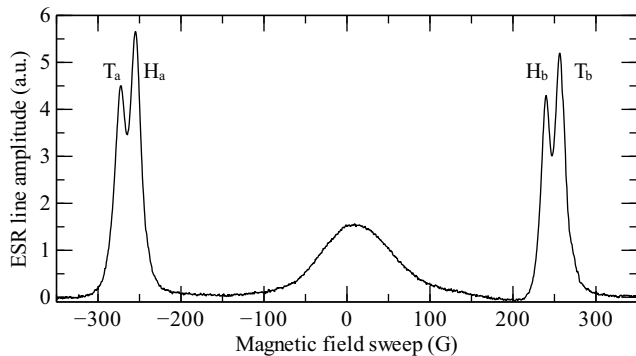


Figure 2. A panorama spectrum of T and H ESR lines of sample 4 stored at 70 mK. Note the difference in T and H line polarization. A broad line of unknown origin appears at the ESR spectrum center

to the hyperfine interaction. The hyperfine splitting between the two lines is ≈ 507 G for H and slightly larger ≈ 541 G for T. A typical ESR spectrum which includes all lines of atomic hydrogen and tritium in $T_2:H_2$ matrices is shown in Fig.2. The spectrum shown corresponds to Sample 4, and is taken after the accumulation of atomic species has been saturated and a maximum density of atomic species is reached. The T:H line ratio was different for various samples. T lines in the samples 1 and 6 were not detected at all, while H lines in the samples 2 and 3 were substantially weaker than T lines. Even though the difference in the hyperfine constants looks relatively large, for the very high densities studied in this work the density dependent broadening was so large that it was not always easy to resolve ESR line of H and T from each other.

At high densities of atoms studied in this work the effects of dipole-dipole interaction between atoms start to play important role and influence the shape and position of ESR lines. It has been shown in our previous work [16] that the dipole-dipole interaction leads to a Lorentzian lineshape with the width linearly increasing as a function of density. This dependence can be used for the absolute determination of atomic density. A second important consequence of high density fully polarized electron spins is a macroscopic magnetization of the sample, which leads to shifts of the ESR lines. This effect depends on the geometry of the sample, and for thin films perpendicular to the main polarizing field the net dipolar field is opposite to the main polarizing field. This leads to the linear density-dependent shift of the ESR lines towards the larger sweep fields, i.e. to the right in the spectra as they are recorded by our technique. Having the possibility of using the H gas lines as absolute field markers, these shifts can be accurately measured and also provide a measure of the absolute density of atoms in the films.

For the high density samples and thick (>350 nm) films another ESR line broadening effect caused by the radia-

tion damping brings extra complications in the analysis of the ESR spectra. The effect of radiation damping is related to spontaneous and coherent emissions of energy stored in the spin system into the resonant cavity at the electron Larmor frequency [25]. It typically occurs in spin systems strongly coupled to the microwave field of the cavity, when the relaxation time due to interaction of spin system with cavity field becomes comparable to the spin-spin relaxation time T_2 , i.e. $T_2 \sim T_{rad} = (2\pi M_0 Q \eta)^{-1}$. Here M_0 is the sample magnetization, Q is the resonator quality factor and η is the resonator filling factor. In this case the effective relaxation time of the system $1/T_2' = 1/T_2 + 1/T_{rad}$. This also results in an additional line broadening proportional to the number of spins in the sample. The radiation damping effect depends on the detuning of the spectrometer frequency from the center of the cavity resonance, and it is possible to reduce it to a negligible level by increasing the detuning to several cavity resonance widths. This was verified for the thickest films of the sample 1, where the effect was strongest. We observed a factor of 2 decrease in the ESR linewidth after such detuning. For all other samples the radiation damping effects were substantially weaker and added not more than 20% to the actual linewidth, which was however taken into account in the analysis.

A typical dependence of the tritium ESR line shift and width on the total atomic density measured for the sample 2 is presented in Fig.3. In the inset we show a real spectrum of the high field line with all three components: T and H lines from the atoms in the film, and the H gas line from the atoms in the bulk of the SC. In this sample the lines from the atoms in the solid are of comparable amplitude and poorly resolved from each other because of their rather large width. The H gas line is very narrow and easily distinguishable in the spectrum. We fitted such lineshapes with three Lorentzian functions, which are also presented in the inset of the Fig.3.

For the measurement of the absolute density of atoms in thin solid films we used known dependence of the ESR line width and shift on density [16]. This dependence was verified during several experimental runs with respect to the calorimetric method of measurement of the absolute number of hydrogen atoms. The calorimetric method is based on the measurement of the energy released in stimulated by ESR recombination of the atoms of the H gas versus the reduction of their ESR signal. This method agreed to within 20% accuracy with calibrations based on the linewidth and shift measurements, and we consider 20% as an upper limit estimate of the error in density determination in this work.

A broad, ~ 100 G wide, line of an unknown nature was observed at the center of the ESR spectrum for all samples studied in this work (Fig.2). The line width and area increased during storage and saturated after one week of measurements. The line remained in the spectrum after the SC cleaning procedure when we raised the SC tem-

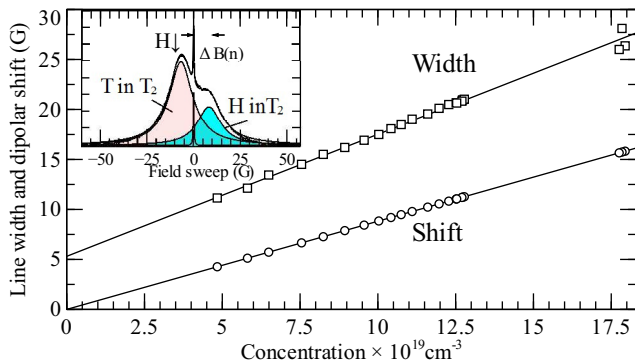


Figure 3. The ESR line width and shift from the H-gas phase line as a function of the atomic concentration. Inset: a typical spectrum of the H and T low field lines fitted by 3 lorentzian curves. The concentration-dependent (dipolar) shift from the H-gas line ($H\downarrow$) is labeled as $\Delta B(n)$ in the inset.

peratures above $\simeq 20$ K and cooled back to 1 K. Since the solid molecular film has been completely removed after such cleaning, it seems that the central line originates from some atoms or free radicals in the metallic mirrors of the Fabry-Perot resonator. We have not observed this line after warming up to room temperature and starting new experimental run. A large area of the central line also implies a large number of the free radicals which produce it, about same as the number of unpaired atoms in our molecular films. A strong broad signal seen at the center of the spectrum in Fig.2 is reminiscent of the central peak seen in the semiconductor Si:P at high phosphorus concentration and was taken to be attributed to the formation of the donor pairs coupled by the strong exchange interaction [26]. The work is continuing in an attempt to fully understand this important observation.

A weak line of trapped electrons similar to that found for other hydrogen matrices [27] was observed in thick T_2 and $T_2:H_2$ samples but it was absent in the films thinner than 100 nm (samples 3 and 4). In our ESR spectra we have not observed any signatures of ions or other species trapped in hydrogen films. The most stable of ions H^+ and H_3^+ (T^+ and T_3^+) have a zero electron spin and cannot be detected by ESR. The yield of other ions, such as H_2^+ (T_2^+) and H_2^- (T_2^-) is expected to be 4 orders of magnitude smaller than for unpaired atoms [28] and lies below our sensitivity threshold.

In addition to the conventional ESR diagnostics we implemented measurements of the Electron-Nuclear Double Resonance (ENDOR) on our samples. The method is based on detecting the frequency of the NMR transition by its influence on the amplitude of the ESR lines. The ENDOR measurement was typically done by sweeping the magnetic field to the center of the ESR line, and then applying the rf excitation to one of the miniature coils located near the sample on the QM electrode. Then the frequency of the rf source was swept slowly near the

expected NMR transition of H or T atoms. The NMR frequencies can be determined as

$$\omega_{NMR} \simeq 2\pi \frac{A}{2} + \gamma B \quad (3)$$

where A is the hyperfine constant of H (1417.3 MHz) or T (1512.6 MHz), γ is the proton or triton gyromagnetic ratio and B is the local magnetic field felt by atoms. A change of the ESR signal was observed when the frequency of the rf source matched the NMR transition. Typical ENDOR spectra recorded by this method are presented in Figs.8 and 10.

III. EXPERIMENTAL RESULTS

A. Pure tritium samples

In our "pure" tritium samples we have not added any extra hydrogen to the tritium gas which we extracted from the vials. Since the analysis showed a 15% HT impurity, we assume that all our "pure" tritium films contained about 15% of HT. This is the smallest hydrogen impurity which could be realized in experiments with tritium, but it is still rather large to assure absence of H atoms in the samples. Our study includes two pure tritium samples, 2 and 3 (Tab.I) with thickness of 250 and 35 nm respectively.

Accumulation of T atoms due to energetic electrons from T-decay in sample 2 recorded at 160 mK is shown in Figs. 4 and 5. Tritium ESR lines appeared almost immediately after film deposition with a width of ~ 5 G. Then, the lines grew rapidly, and already after about 3 hours we observed an abrupt decrease in the accumulated density accompanied by the increase in the QM frequency. Further accumulation was interrupted several times with similar events at 3×10^4 and a substantially larger change at around 10^5 sec on the time scale of Fig. 4. These changes in the ESR and QM signals were accompanied by spikes in the SC temperature up to ~ 250 mK, and indicate explosive recombination of part of the sample. Later on the explosive events occurred for nearly equal time intervals, and with reproducible changes of the atomic density from $\approx 1.6 \times 10^{20} \text{ cm}^{-3}$ to $\approx 1.2 \times 10^{20} \text{ cm}^{-3}$. Occasionally the explosions were triggered by the SC overheating during sweeps of magnetic field between ESR lines. The T:H ratio did not change after the explosions.

Accumulation of the atomic densities in the much thinner (35 nm) Sample 3 followed monotonically increasing function which saturated at a total density of $\approx 1.2 \times 10^{20} \text{ cm}^{-3}$ and remained stable at temperatures down to 70 mK for the observation time of several days. No explosive recombination events were seen for Sample

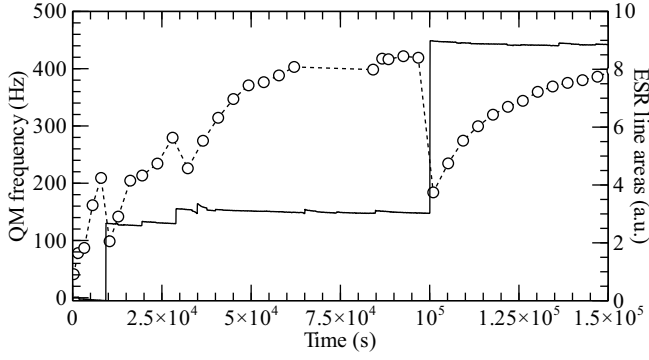


Figure 4. Accumulation of atomic concentration in the sample 2 (circles), and QM response on explosive recombination of atoms in sample 2.

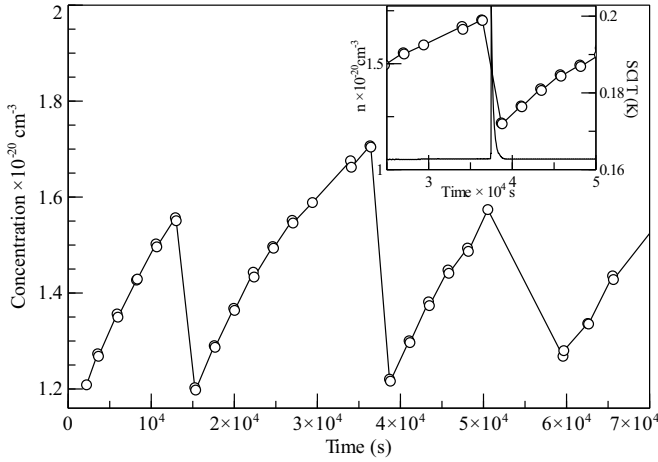


Figure 5. Time evolution of the total T and H atomic concentration in sample 2 stored at 160 mK. The explosive recombination events presented here appear spontaneously. Inset: the sample cell temperature spike during one of such events.

3. Smaller concentrations in the thinner film can be explained by less efficient accumulation of atoms because the high-energy electrons escape from the film carrying substantial part of their energy, which is not used for dissociation.

Signals of atomic hydrogen behaved similarly to those of T in both samples, but the total area of H ESR lines was 6 to 10 times smaller than that for the T lines. This roughly corresponds to the T:H atomic ratio in the gas mixture prior to condensing and did not change during the course of measurement. This means that the majority of H atoms in these samples were created by direct dissociation of HT molecules while the isotopic exchange reaction $T + HT \rightarrow T_2 + H$ is quite inefficient and does not lead to significant T-H conversion.

A zero-concentration or matrix width of ≈ 5 G for H and T lines in pure normal T_2 can be found as an offset on the vertical axis of the width vs. density plot (see Fig.3). This value is substantially larger than that

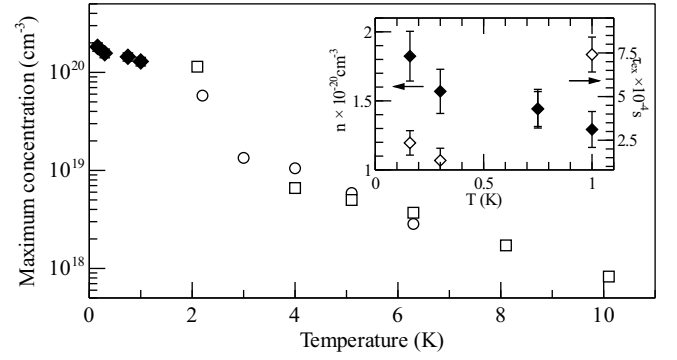


Figure 6. Maximum concentrations of unpaired atoms obtained in our work and in previous works using tritium disintegration. Present work (sample 2) T in T_2 (black diamonds), T in T_2 [7] (open squares), D, T in D-T matrix (50% DT, 25% D_2 and 25% T_2) [7] (open circles) Inset: Dependence of atomic concentration on storage temperature (sample 2) black diamonds and dependence of average period of explosive recombination events on storage temperature: open diamonds. The inset data was measured in sample 2

in $n\text{-H}_2$ (1.1 G). The line broadening due to ortho- T_2 molecules should rapidly vanish due to the fast ortho-para conversion which is catalysed by high concentration of atoms. The conversion should proceed for the molecules in the closest neighbourhood of T and H atoms with a time constant of about 10 s and to be of order of $\approx 10^3$ s for the whole sample [29]. We suggest that the main contribution to the matrix width of H and T in our T_2 samples comes from a large HT impurity. A HT molecule is composed of distinguishable atoms and the magnetic moments of a proton and triton may contribute to the line broadening. The matrix width for unpaired atoms in HD, 2.8 G is known to be larger than that in $n\text{-H}_2$ (1.1 G) and $o\text{-D}_2$ (1.3 G). Taking into account that the deuteron magnetic moment is about 3.5 times smaller than that of T, one may expect a nearly 2 time larger matrix width in pure HT than in HD and some fraction of that in our samples.

Recombination explosions of unpaired atoms were studied at different temperatures: 300, 750 mK and 1 K. (see Fig.6). Increasing the temperature slowed down growth of density as the recombination rate increased. The heat spikes were observed at all three temperatures, but the time intervals between the spikes greatly increased and changed from about 2×10^4 s at 160 and 300 mK to 8×10^4 s at 1 K. This trend agrees with the results obtained previously by Collins et al. [7, 11] who observed the heat spikes in their bulk $H_2 + 2\% T_2$ samples at 1.2 K and reported on their absence at 2 K. Storing the sample at higher temperatures also resulted in smaller atomic concentrations reached. Similar results were also found by Collins et al. [7] who reported on gradual decrease of atomic concentrations while raising the storage temperature from 2.1 to 10 K.

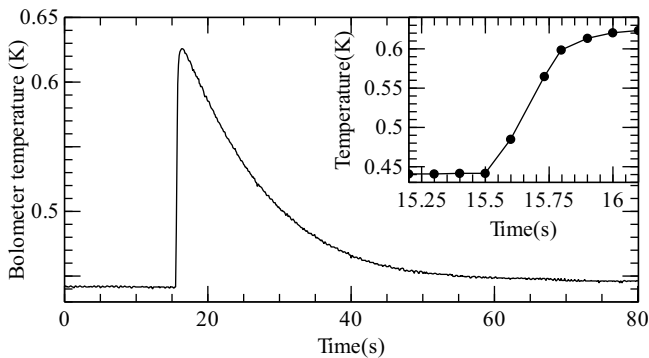


Figure 7. Bolometer response on the explosive recombination of atoms in sample 2. The bolometer temperature jump due to thermal explosion is zoomed in the inset

We studied the onset of thermal explosions using a Ru-oxide bolometer which was arranged in the upper volume of the SC near the QM surface with the samples. The bolometer temperature was somewhat higher than the SC temperature due to heating by excitation during measurement and noise pick-up (Fig.7). The bolometer temperature increased significantly during explosive recombination from 0.4 K to almost 0.65 K which is much higher than the cell temperature at the same time. There are two possible ways of heating the bolometer: condensation of hot tritium and hydrogen molecules onto it or by means of radiation similar to that observed by Mapoles et al.[12]. The bolometer temperature after each event of explosive recombination recovered to slightly higher reading which brings evidence of re-condensing T_2 onto it.

Although the thermal response of the bolometer to the heat spikes is substantially faster than that of the sample cell, neither of them is fast enough to follow the actual time evolution of the recombination explosions. From the bolometer response we can conclude that the explosion event develops in the time scale faster than ~ 0.1 s. Mapoles et al. detected flashes in bulk D-T samples which were attributed to explosive recombination of atoms[12]. The flashes they observed developed within ≤ 1 ms which can be assumed as an upper limit for formation of a heat spike. We were not able to resolve such fast events with the technique available in these experiments.

We tried to measure the energy released in the explosions by simulating a heat spike with heat pulses applied to the resistive heater attached to the sample cell body. This was done by adjusting the strength and duration of the heat pulses to obtain the same SC thermometer response as was detected during explosive recombination. We observed the same response using a 17 ms and $P \simeq 22$ mW pulse. Then, calculating the total energy released by such pulse we evaluated the number of recombined atoms which would produce such energy

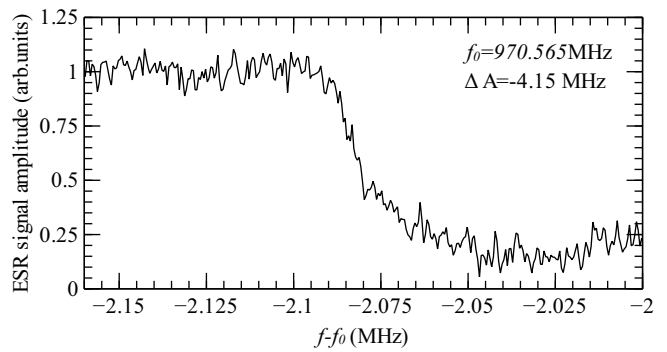


Figure 8. ENDOR of atomic tritium in a T_2 matrix. The calculated transition frequency for atoms in the gas phase is denoted as f_0

bursts as 1.0×10^{15} . This number matches well the decrease in atom number 9.0×10^{14} measured by our ESR technique. A good agreement between these two numbers also proves good accuracy of our calibration of the absolute density as a function the ESR line width and area.

Accumulation of unpaired atoms in solid T_2 can be described by a simple model based on a second-order differential equation (4)

$$\frac{d[T]}{dt} = 2F[T_2] - K_T^r[T]^2, \quad (4)$$

where $[T]$ and $[T_2]$ are the concentrations of tritium atoms and molecules, F is the production rate (dissociation probability per second) of T-atom pairs and K_T^r is the temperature dependent recombination constant. Both production rate and temperature dependent recombination can be extracted by fitting the density growth rate, $\frac{d[T]}{dt}$, with a square function and keeping F and K_T^r as fitting parameters. Using the value of F extracted from the fit to the data of Sample 2 we estimated that each electron released after β -decay of T creates ~ 50 unpaired H or T atoms. This result is in a fair agreement with that of Collins et al. [7] who found that the production efficiency at 2.1 K is about 70 atoms per disintegration event [7]. However this value is larger than that reported by Sharnoff and Pound: 22 unpaired atoms in their D_2 samples [9].

Measuring the spectra of electron-nuclear double resonance (ENDOR) in “pure” T_2 samples we found a clear transition at ≈ 2.085 MHz lower frequency than the value calculated for free atoms (see Fig.8). This corresponds to a negative change of the hyperfine constant, similar to what has been observed for H in solid H_2 and D_2 matrices. We carefully checked the frequency range a few MHz above the free atom value, but no other transitions were detected there. This result agrees with the previous results by Lambe [8] and Sharnoff and Pound [9] but contradicts to the data of Collins et al. [7] who reported

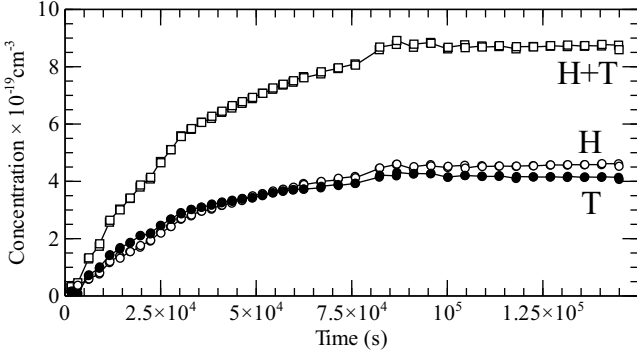


Figure 9. Time evolution of H and T concentrations in the sample 4 stored at 80 mK

a large positive increase of the hyperfine constant for T atoms in a T_2 matrix.

B. Tritium:hydrogen mixtures

We studied three $T_2:H_2$ mixture samples (Samples 4,5,6). The maximum concentration of atomic hydrogen was achieved in the Sample 5: $1.1 \times 10^{20} \text{cm}^{-3}$. However only modest concentrations, $\sim 5 \times 10^{19}$ and $\simeq 2.5 \times 10^{19} \text{cm}^{-3}$ were achieved in the 4th and 6th samples (Tab.I). The T:H ratios in all three samples were much smaller than one would expect from the ratio of T:H atoms in the gas mixture used for preparing the samples. This gives evidence of a fast T-to-H conversion due to the isotopic exchange reaction (1).

The kinetics of the isotopic exchange reactions (1) and (2) was studied in the 80 nm $T_2:H_2$ sample 4. The time evolution of H and T concentrations in this sample is shown in Fig.9. The H and T lines appeared few minutes after deposition and had equal amplitudes. A nearly 1-to-1 ratio of their areas remained for the whole measurement and can be explained by the very fast reaction (1). A weak increase of the H:T ratio after $t=80000$ s while the total $[H]+[T]$ concentrations remained conserved can be explained by the contribution from the reaction (2). Based on that we concluded that the reaction (2) indeed proceeds much slower and we can neglect its contribution to the $[H]$ growth for our estimate of the rate of the faster exchange reaction (1).

The evolution of T and H atomic concentrations can be expressed by the differential equations:

$$\frac{d[T]}{dt} = 2F([T_2] + \frac{1}{2}[HT]) - K^{ex}[T][H_2] - K_T^r[T]^2 - K_{TH}^r[T][H] \quad (5)$$

$$\frac{d[H]}{dt} = 2F([H_2] + \frac{1}{2}[HT]) + K^{ex}[T][H_2] - K_H^r[H]^2 - K_{TH}^r[T][H] \quad (6)$$

where K^{ex} is a second-order rate constant of the exchange reaction (1) and K^r are the recombination rate constants. The production of H atoms includes two terms: dissociation of H_2 and HT molecules by β -particles and the isotopic exchange reaction (1). If we consider the initial part of the measurement immediately after the deposition of the film, the concentrations of atoms are close to zero and we have only the first terms in equations, e.g. production due to the dissociation. Due to the much larger concentration of T_2 in the sample, we should observe a proportionally larger rate of the atomic $[T]$ growth with respect to $[H]$. As one can see from Fig.9, both $[T](t)$ and $[H](t)$ curves start with the same slope and the densities of T and H are equal to each other during the whole measurement. This implies that the exchange term in equations grows faster than we can observe with our ESR technique, and the exchange reaction (1) occurs on the time scale $\tau^{ex} < 100$ sec, a typical time interval between sweeps of ESR lines. Having $[H]=[T]$ in the course of measurement allows us to fit the rate of the H atom growth, $\frac{d[H]}{dt}$ with a parabolic function, $f(x) = k + k^{ex}x - k^rx^2$, where $x \equiv [T], [H]$, $k = 2F([H_2] + \frac{1}{2}[HT])$ is a constant representing the rate of production, $k^r = K_{TH}^r + K_H^r$ is the effective recombination constant, $k^{ex} = K^{ex}[H_2]$. From the data of Fig.9 we extracted the values for K^{ex} and k^r $3(2) \times 10^{-26} \text{cm}^3 \text{s}^{-1}$ and $10(5) \times 10^{-25} \text{cm}^3 \text{s}^{-1}$, respectively. The relatively large error in these rate constants is caused by a large uncertainty in the concentration of H_2 in our mixtures. Such uncertainty appears due to the small amount of tritium gas we worked with ($\sim 5 \mu\text{mol}$) which created difficulties in preparing $T_2:H_2$ mixtures with a small admixtures of H_2 . The exchange reaction rate found here is smaller than that calculated by Aratono [19] ($2 \times 10^{-25} \text{cm}^3 \text{s}^{-1}$), while the recombination rate agrees with that found in pure T_2 samples. The recombination constant of tritium atoms obtained by Collins et al. [7] is $K_0 = 1 \times 10^{-24} \text{cm}^3 \text{s}$ at 2.1 K.

Estimating the rate of the slower exchange reaction (2) requires a more sophisticated analysis because the differential equations (5) and (6) will contain more terms. Also a longer measurement might be required.

IV. DISCUSSION

We studied several samples of atomic tritium and hydrogen stabilized in matrices of T_2 and $T_2:H_2$. The maximum concentrations of H and T atoms were limited by their recombination. Recombination of atomic hydrogen in solid hydrogen matrices at low temperatures proceeds in two steps: a diffusion stage when atoms approach each other by the distance of a lattice constant followed by rapid recombination into molecules. Kumada[30] showed that diffusion of hydrogen atoms at temperatures $\simeq 1$ K

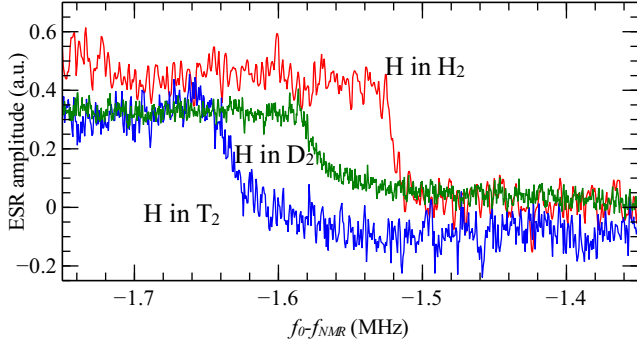


Figure 10. ENDORs of H atoms in matrices of hydrogen isotopes. The calculated transition frequency for H atoms in the gas phase is denoted as f_0

proceeds in a series of exchange tunneling reactions



Similar exchange reaction also governs diffusion of atomic deuterium in solid D_2 , and is also expected in tritium. However its rate should be much smaller than those for hydrogen and deuterium due to a larger mass and smaller zero-point energies of the reactants. The rate of the gas phase reaction (7) at 4.2 K, $k \sim 10^{-25} \text{cm}^3 \text{s}^{-1}$, was calculated by Takayanagi et al.[31] and is in a fair agreement with the recombination rates of H atoms in solid H_2 . The measured recombination rates for D atoms in D_2 are about 2 orders of magnitude smaller than those for hydrogen[32]. Based on that, we may expect that the recombination rates of T atoms in pure T_2 at the same temperatures should be at least 1-2 orders of magnitude smaller than those for D in D_2 .

The reaction (7) and its isotopic analogs have a large activation barrier, $E_a \simeq 4600 \text{ K}$, and proceed at low temperatures by tunneling. Any impurity or crystal defect can perturb the periodic potential of the matrix and create an energy level mismatch for a tunneling event. The mismatch can be compensated by phonons. Ahokas et al.[16] reported enhancement of recombination rate during recombination of gas-phase H atoms at the surface of their H_2 samples. The recombination rates of T atoms in our samples, $k \sim 10^{-24} - 10^{-25} \text{cm}^3 \text{s}^{-1}$, are much larger than what could be expected from the rates of the isotopic exchange reaction $\text{T} + \text{T}_2 \rightarrow \text{T}_2 + \text{T}$ which should have a rate at least 3 orders of magnitude smaller than the value we obtained. This is an upper limit estimate for this exchange reaction in the absence of any limiting factors such as energy level mismatch due to crystal defects. An alternative way can be a physical diffusion of T atoms related to formation of vacancies. Gaines et al. [33] estimated the activation energy for physical diffusion of T in T_2 as 411 K which is about 2 times larger than that for H in H_2 (195 K)[34]. Based on that, one may expect a cross-over temperature from quantum dif-

fusion to Arrhenius-like behavior to be about 2 times larger for tritium than that for hydrogen: about 9 K against 4.5 K. The pre-exponential factors for these processes were found to differ only by a factor of 6 [33], [34] which does not influence the result.

Much higher concentrations of T atoms in “pure” T_2 Sample 2 compared to T_2 samples with H_2 admixtures (4,5,6) leads us to expect a faster recombination of H atoms compared to T. Analysing the differential equations for the evolution of $[\text{H}]$ and $[\text{T}]$ concentrations in the T_2 sample 3 and T_2 : H_2 sample 6 we obtained a 3 times larger recombination rate for H atoms in the latter sample.

β -decay of tritium results in the formation of a large number of non-equilibrium vacancies and phonons which may lead to a significant enhancement of physical diffusion. Ebner and Sung [35] considered two cases of diffusion through vacancies in H_2 : tunneling and hopping to the empty sites. Pure tunneling of a T or H atom in a T_2 matrix should be suppressed due to a large number of lattice defects but it can be enforced by phonons generated by tritium decay. The phonons may not only help to compensate for the energy level mismatch but also help atoms to hop over the barrier and stimulate physical diffusion followed by recombination. Due to the very large energy released in the tritium decay the real temperature of phonons may be much higher than the typical storage temperatures $\sim 100 \text{ mK}$ used in our experiments. Recombination of atoms brings extra heating, which leads to enhancement of diffusion and recombination rate at higher densities of atoms. Such positive feedback in the system finally leads to a thermal explosion of atoms which occurs at a certain critical density. At high enough concentration of atoms even a small increase of temperature may cause an instantaneous increase of number of phonons and provoke a so-called stimulated explosion.

The fact that only a fraction of atoms in the film recombines during explosions may probably be explained by better stability of atoms more close to the film substrate due to better cooling whereas the atoms closer to the top of the films recombine preferentially. This also explains the absence of thermal explosions in thin films and their suppression after adding helium to the sample cell which provides better cooling to the upper surface of the film.

We tried to estimate possible overheating of the tritium film during a recombination explosion using a simple heat balance model. We assume that the heat released in a recombination event is conducted by the phonons from the T_2 film to the quartz microbalance and further down into the SC lower volume, where part of the recombination energy is removed by sublimation of tritium molecules. From the frequency change of our QM we know that $\approx 5\%$ of the T_2 film becomes sublimated after typical explosive recombination when the density of atoms is decreased by

$4 \times 10^{19} \text{ cm}^{-3}$ (see Fig.5) corresponding to recombination of $\sim 10^{15}$ atoms. Taking the sublimation heat of solid T_2 , $H=1400 \text{ J/mol}$ [22], we evaluate that about 1/3 of energy released in recombination of atoms is removed from the sample by the sublimated molecules. The rest of the energy is conducted into the lower volume of the SC and passes through several boundaries between solid hydrogen and gold electrode, gold-quartz and finally gold-helium interfaces. It turns out that the boundary thermal resistance between gold electrode and T_2 film becomes the bottleneck for cooling the sample. The boundary thermal resistances for gold-quartz and solid T_2 -gold interfaces were calculated using the acoustic mismatch model, which agreed with a factor of 2 with experimental values [36]. The temperatures for all layers of the microbalance: both gold electrodes and the quartz were estimated by a simple model, similar to the estimate by Wyatt[37] using the equations:

$$\dot{q} = G_{ij} A (T_h^n - T_c^n)$$

Here G_{ij} is the thermal boundary conductance between interfaces i and j (e.g. solid hydrogen and gold), A is the QM surface area (1 cm^2), $n=4$ for the solid-solid interfaces and $n=5$ for the interfaces between liquid helium and solids. T_h and T_c are the temperatures of the hotter and colder layers respectively. For the estimate of the heat power \dot{q} we need to know the time duration of the recombination explosion event. From our bolometer response we obtain the value of $\tau_{rec} \lesssim 100 \text{ ms}$, while the light flashes observed by Mapoles et. al.[12] indicate that it can be shorter than 1 ms . Using the heat conductance model above for the duration of the recombination explosion of 1 ms we evaluate overheating of the tritium film to $\sim 16 \text{ K}$, and $\sim 12 \text{ K}$ if the explosion occurs during 10 ms . Both temperatures are high enough to evaporate solid tritium, and for substantial enhancement of the rate of the physical diffusion of T atoms.

Analysis of our data from ENDOR measurements allows making certain conclusions about the structure of the tritium films we studied. The lattice structure is estimated from the influence of the host molecules on the electron clouds of unpaired atoms. Depending on a lattice site either a long-range attractive van-der-Waals interaction or a short-range Pauli repulsion prevails. A negative change of the hyperfine constant corresponds to the substitutional lattice sites where the attractive van-der-Waals contribution takes over. In this work we observed a single ENDOR transition for T atoms in solid T_2 corresponding to a $\approx -4.15 \text{ MHz}$ shift of the hyperfine constant with respect to the free atom transition. We have also performed ENDOR measurements for H atoms in a T_2 matrix. We present it in Fig.10 together with the spectra in the matrices of H_2 and D_2 for the sake of comparison. The change of the hyperfine constant of H atoms stabilized in a T_2 matrix was found to

be -3.17 MHz which is about 0.1 MHz larger compared to that of H atoms in the matrices of other hydrogen isotopes. Tritium molecules have the lowest zero-point energy among the hydrogens and so the lattice constant for solid T_2 is the smallest as compared to the other isotopes. The H atoms placed in more quantum matrices of lighter hydrogens are pushed further away by the molecules and the hyperfine constant is closer to that of free atoms. This also explains why the shift of the ENDOR transition of H in T_2 is larger than in H_2 . Observation of a single ENDOR transition in all four cases indicates that the impurity atoms occupy the same substitutional site in the lattice, and the lattice type is most likely the same for all matrices.

V. CONCLUSIONS

In conclusion, we reported on the first ESR study of T and H atoms stabilized in “pure” T_2 and $\text{T}_2:\text{H}_2$ matrices at temperatures down to 70 mK . The concentrations of T atoms approaching $2 \times 10^{20} \text{ cm}^{-3}$ were reached in pure T_2 films. The record-high concentrations of H atoms $\sim 1 \times 10^{20} \text{ cm}^{-3}$ were reached in $\text{T}_2:\text{H}_2$ solid mixtures. It turned out that the isotopic exchange reaction $\text{T} + \text{H}_2 \rightarrow \text{HT} + \text{H}$ proceeds with a much higher efficiency compared to reaction $\text{T} + \text{HT} \rightarrow \text{T}_2 + \text{H}$ and results in a spectacular T-to-H conversion in $\text{T}_2:\text{H}_2$ mixtures. The accumulation of H and T atoms was limited by their recombination which also occurred in an explosive manner depending on the storage conditions. We suggest that the main mechanism for H and T migration in solid T_2 is physical diffusion related to tunneling or hopping to vacant sites in the lattice in contrast to isotopic chemical reactions which govern diffusion of H and D atoms created in H_2 and D_2 matrices by other methods.

We acknowledge funding from the Wihuri Foundation and the Academy of Finland grants No. 258074, 260531 and 268745. This work is also supported by NSF grant No DMR 1209255. S.S. thanks UTUGS for support.

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